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(54) Title: CROSSLINKABLE ETHYLENE POLYMER BLENDS

(57) Abstract: Novel polymer blends are provided comprising crosslinkable polymeric composition comprising (a) A blend of: (i) 100 parts by weight of LDPE component (A) (ii) 1-200 parts by weight of HDPE component (B) having a polydispersity (M_w/M_n) of <12. (iii) 0-100 parts by weight of an EVA copolymer (C). Particularly preferred compositions comprise blends having HDPE components having a polydispersity of <7. The blends are particularly suitable for use in automotive cables together with flame retardants and antioxidants. The crosslinked cables show an acceptable combination of improved temperature resistance and mechanical properties, abrasion resistance, reduced halogen content, ease of use and processability.

CROSSLINKABLE ETHYLENE POLYMER BLENDS

The present invention relates to novel polymer blends and in particular to blends particularly suitable for use as components of cross-linkable compositions for use as automotive cables. The novel polymer blends allow such cross-linkable compositions to impart improved mechanical properties and processability in such cables.

5 At present automotive cables are commonly insulated with polyvinyl chloride and are designed to service temperatures of 100°C. However, increased working temperatures and reduced space under automobile bonnets have led the industry to increase the service temperature of automotive wires. In order to meet the new criteria of higher temperatures, for example in the range 105 - 125°C, automotive wires need to
10 exhibit improved thermal resistance. As a consequence of this increased service temperature and the drive to reduce the use of chlorinated compounds in automobile manufacturing, polyvinyl chloride (PVC) is no longer a preferred material for automotive wiring.

In addition to the thermal resistance requirement of the new automotive
15 specifications, the wires must also offer high mechanical properties, high abrasion resistance, excellent resistance to oils and solvents and resistance to fire.

The known alternatives to PVC for the insulation of automotive wires, suffer from several drawbacks. Compounds based on halogen free retardants suffer from poor processability and inferior mechanical properties compared to PVC compounds. Sioplas
20 compounds whether halogen-free or halogenated suffer from poor shelf life which can give rise to gel problems during extrusion.

It is one of the objects of the present invention therefore to provide a suitable

resin system for automotive cables having an acceptable combination of improved temperature resistance and mechanical properties, abrasion resistance, reduced halogen content, ease of use and processability.

US 5439965 describes polymeric compositions useful as insulation for wire and cable products for example automotive applications. In particular crosslinkable polymeric compositions comprising copolymers of ethylene and vinyl esters are disclosed in combination with flame retardant materials. Similar materials are described in US 4477523 and US 4255303.

US 4035325 describes flame retardant combinations of antimony trioxide and hexabromocyclododecane improved by the addition of certain organometallic compounds.

It has now been discovered that novel blends comprising high density polyethylenes (HDPE) having polydispersity (M_w/M_n) of < 12 may be suitably used as components of cross-linkable polymeric compositions for use as automotive cables. In particular novel polymer blends comprising such HDPE with a low density polyethylene (LDPE) and optionally an ethylene vinyl acetate (EVA) component have been developed.

Thus according to the present invention there is provided a crosslinkable polymeric composition comprising a blend of:

- 20 (i) 100 parts by weight LDPE component (A)
- (ii) 1 – 200 parts by weight HDPE component (B) having a polydispersity (M_w/M_n) of < 12, and
- (iii) 0 - 100 parts by weight of an EVA component (C).

A preferred composition comprises a blend of:

- 25 (i) 100 parts by weight LDPE component (A)
- (ii) 1 – 100 parts by weight HDPE component (B) having a polydispersity (M_w/M_n) of < 12, and
- (iii) 0 - 100 parts by weight of an EVA component (C).

A highly preferred composition comprises a blend of:

- 30 (i) 100 parts by weight LDPE component (A), and
- (ii) 1 – 60 parts by weight HDPE component (B) having a polydispersity (M_w/M_n) of < 12.

A particularly preferred composition comprises a blend of:

- (i) 100 parts by weight LDPE component (A), and
- (ii) 25 - 55 parts by weight HDPE component (B) having a polydispersity (Mw/Mn) of < 12.

5 A most preferred composition comprises a blend of:

- (i) 100 parts by weight LDPE component (A), and
- (ii) 35 - 55 parts by weight HDPE component (B) having a polydispersity (Mw/Mn) of < 12.

The LDPE component (A) has a density in the range 0.918 - 0.940 g/cm³,
10 preferably a density in the range 0.923 - 0.940 g/cm³, most preferably a density in the range 0.926 - 0.940 g/cm³, and even more preferably a density in the range 0.930 - 0.940 g/cm³.

The LDPE component (A) has a MFR in the range 0.1 - 3 g/10 minutes, more
15 preferably a MFR in the range 0.15 - 2 g/10 minutes, and most preferably a MFR in the range 0.5 to 1.5 g/10 minutes.

The HDPE component (B) has a density in the range 0.940 to 0.965 g/cm³,
preferably a density in the range 0.940 - 0.960 g/cm³, and most preferably a density in
the range 0.950 - 0.960 g/cm³.

The HDPE component (B) has a MFR in the range 1 - 10 g/10minutes, and
20 preferably a MFR in the range 2 - 6 g/10minutes,

The preferred HDPE component (B) has a polydispersity (Mw/Mn) < 9 and a
particularly preferred polydispersity (Mw/Mn) < 7.

The EVA component (C) has a vinyl acetate (VA) content in the range 1 - 45 %
by weight and a MFR in the range 0.1 - 50 g/10 minutes.

25 The LDPE, HDPE and EVA copolymer may suitably be prepared using well known polymerisation catalysts and processes.

The melt flow rate (MFR) measurements are made according to ISO 1133 condition D and density measurements are made according to ISO 1183 method D. Weight average molecular weight (Mw) and number average molecular weight (Mn)
30 were measured by Gel Permeation Chromatography (GPC) using a Waters 150C instrument using a mobile phase of 1,2,4-trichlorobenzene at 140°C. Sample solutions were made by dissolving the polymers in the same solvent. All solutions were tested

without filtering. Molecular weights were calculated as polyethylene equivalents. The polydispersity is defined as the ratio of Mw to Mn.

When used in combination with an antioxidant system (D) and a flame retardant package (E) the novel blends of the present invention result in crosslinkable polymeric compositions having the required combination of properties suitable for use as automotive cables having a reduced halogen content compared to PVC.

Thus according to another aspect of the present invention there is provided an automotive cable comprising a crosslinkable polymeric composition comprising

(a) a blend of

- 10 (i) 100 parts by weight LDPE component (A)
- (ii) 1 - 200 parts by weight HDPE component (B) having a polydispersity (Mw/Mn) of < 12, and
- (iii) 0 - 100 parts by weight of an EVA copolymer (C).

(b) an antioxidant system (D), and

15 (c) a flame retardant material (E).

A preferred crosslinkable composition comprises a blend of:

- 10 (i) 100 parts by weight LDPE component (A)
- (ii) 1 - 100 parts by weight HDPE component (B) having a polydispersity (Mw/Mn) of < 12, and
- (iii) 0 - 100 parts by weight of an EVA copolymer (C).

A highly preferred crosslinkable composition comprises a blend of:

- 20 (i) 100 parts by weight LDPE component (A), and
- (ii) 1 - 60 parts by weight HDPE component (B) having a polydispersity (Mw/Mn) of < 12.

25 A particularly preferred crosslinkable composition comprises a blend of:

- 25 (i) 100 parts by weight LDPE component (A), and
- (ii) 35 - 55 parts by weight HDPE component (B) having a polydispersity (Mw/Mn) of < 12.

A most preferred crosslinkable composition comprises a blend of:

30 (i) 100 parts by weight LDPE component (A), and

- (ii) 25 - 55 parts by weight HDPE component (B) having a polydispersity (Mw/Mn) of < 12.

The preferred LDPE and HDPE suitable for use in the crosslinkable compositions according to this aspect of the present invention have the densities and MFR described above.

5 The preferred HDPE have a polydispersity of < 9 and most preferably < 7.

The antioxidant used as component (D) may be any conventional material but is preferably a combination of well known IrganoxTM materials. A combination of IrganoxTM 1010 and IrganoxTM MD1024 has been found to be particularly useful in the present invention.

10 A preferred antioxidant for use in the present invention comprises a mixture of Irganox MD 1024TM of concentration between 0.1 – 0.9 parts per hundred by weight of polymer blend and Irganox 1010TM of content 0.2 - 0.9 parts per hundred by weight of polymer blend. A particularly preferred antioxidant package comprises a mixture of Irganox MD 1024TM of concentration between 0.1 – 0.6 parts per hundred by weight of polymer blend and Irganox 1010TM of content 0.2 - 0.6 parts per hundred by weight of polymer blend.

15 The flame retardant package (E) may be comprised of any conventional halogenated materials. As part of the flame retardant package (E) optionally a coagent may be used for increased efficiency of the flame retardant additive. Examples of suitable brominated agents are aromatic or aliphatic compounds typically containing an amount of bromine in the range 70 – 90 %. Typical examples include polybrominated diphenyl ethers, hexabromocyclododecane, ethane-1,2-bis(pentabromophenyl), tetrabromophthalate diols and polyethers, tetrabromobisphenol A and derivatives. Typical examples of coagents include antimony trioxide, Zinc sulphide, Zinc oxide, Zinc borate and boric acid.

25 A particularly preferred flame retardant package for use in the present invention comprises a coagent of content 3 – 28 parts per hundred by weight of polymer blend and a brominated additive of content 9 - 55 parts per hundred by weight of polymer blend, most preferably with a coagent content of 6 – 20 parts per hundred by weight of polymer blend and a brominated additive of content 15 - 40 parts per hundred by weight of polymer blend.

The use of such a flame retardant package provides limited interference with the crosslinking and extrusion properties of the novel polymer blend and allows the

mechanical properties and abrasion requirements of automotive cables to be achieved.

The polymeric composition may be extruded and crosslinked by use of a one or two step silane crosslinking process, a peroxide crosslinking process or an irradiation crosslinking process. Optionally a promoter to enhance irradiation crosslinking may be incorporated.

Suitable one step silane procedures include dry silane or liquid silane injection and the two step silane procedure may be the Sioplas™ process described in US 3646155. Crosslinking procedures are well known and may be illustrated in EP 426073.

The present invention will now be further illustrated by reference to the following examples:

Example 1: Novel Blend Formulation

Blend Component	Parts by weight
LDPE: MFR =1 g/10minutes, Density= 0.934 g/cm ³	100
HDPE: MFR =4 g/10minutes, Density= 0.960 g/cm ³ , density, Mw/Mn=6	82

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Example 2: Novel Blend Formulation

Blend Component	Parts by weight
LDPE: MFR =1 g/10minutes, Density= 0.934 g/cm ³	100
HDPE: MFR =4 g/10minutes, Density= 0.960 g/cm ³ , Mw/Mn =6	50

Example 3: Novel Blend Formulation

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Blend Component	Parts by weight
LDPE: MFR =1 g/10minutes, Density= 0.934 g/cm ³	100
HDPE: MFR =4 g/10minutes, Density= 0.957 g/cm ³ , Mw/Mn =6	50

Example 4: Novel Blend Formulation

Blend Component	Parts by weight
LDPE: MFR =1 g/10minutes, Density= 0.934 g/cm ³	100
HDPE: MFR =4 g/10minutes, Density= 0.957 g/cm ³ , Mw/Mn =6	43

Example 5: Novel Blend Formulation

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Blend Component	Parts by weight
LDPE: MFR =1 g/10minutes, Density= 0.934 g/cm ³	100
HDPE: MFR =4 g/10minutes, Density= 0.954 g/cm ³ , Mw/Mn =5	60
EVA copolymer, MFR =4.5 g/10minutes, 24% weight VA	20

Example 6: Use of Novel blends as components of silane crosslinked automotive cables

The novel polymer blends above when compounded with an antioxidant system and flame retardant package indicated below:

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Composition	Parts by weight
Novel Polymer blend (example 1 - 5)	100
Irganox MD 1024	0.6
Irganox 1010	0.6
Antimony trioxide	14.5
decabromodiphenyl oxide	28.9

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using a twin screw extruder (40 mm, 21 L/D, counter-rotating) with the following compounding settings:

Settings	
Temperature zone 1 (°C)	160
Temperature zone 2 (°C)	175
Temperature zone 3 (°C)	180
Temperature zone 4 (°C)	190
Temperature zone 5 (°C)	190
Temperature zone 6 (°C)	190
Temperature zone 7 (°C)	190
Output (kg/h)	15

5 give formulations suitable for use as a crosslinkable automotive formulation.

These formulations when extruded on a 45 mm 24 L/D extruder with addition of 2 % of Dry Silane masterbatch 7030 DS 80 from PolyOne (one step silane crosslinking) give wires suitable for use in automotive cables.

- Extruder temperatures (°C):

Z1	Z2	Z3	Z4	Z5	Z6	Head	Die	Screw
150	160	175	210	230	240	240	250	80

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- screw design : Elise
- extrusion tools : 3 angle die and wire guide
- speed of the line : 50 m / min
- thickness of the insulating layer : 0.3 mm
- diameter of the copper core : 0.8 mm
- temperature of the compound at the entrance of the feed zone : cold (23 °C)
 - temperature of the cooling trough : 60 °C

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3 - Cable properties:

Crosslinking performance in air (according to IEC 811-2-1):

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After 4 hours in water at 80°C :

Hot set test at 200 °C, 20 N/cm² (%): <150%

Mechanical properties before ageing (according to IEC 811-1-1):

Tensile stress at break (MPa)	>12
Elongation at break (%)	>300

Winding test after ageing 10 days @ 150°C on copper (according to IEC 811-1-2):

5 No cracks

Flame test (according to ISO 6722):

Pass

Scrape abrasion resistance (according to ISO 6722):

Number of cycles before failure : > 300

10 Example 7: Use of Novel blends as components of irradiation crosslinked automotive cables

The novel polymer blends above when compounded with an antioxidant system and flame retardant package indicated below:

Composition	Parts by weight
Novel Polymer blend (example 1 - 5)	100
Irganox MD 1024	0.6
Irganox 1010	0.6
Silica supported triallylcyanurate (TAC). Contains 70% triallylcyanurate.	5.3
Antimony trioxide	15.2
decabromodiphenyl oxide	30.4

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using a twin screw extruder (40 mm, 21 L/D, counter-rotating) using the following compounding settings:

Settings	
Temperature zone 1 (°C)	160
Temperature zone 2 (°C)	175
Temperature zone 3 (°C)	180
Temperature zone 4 (°C)	190
Temperature zone 5 (°C)	190
Temperature zone 6 (°C)	190
Temperature zone 7 (°C)	190
Output (kg/h)	15

5 give formulations suitable for use as an irradiation crosslinkable automotive formulation.

These formulations when extruded on a 45 mm 24 L/D extruder under the following conditions and crosslinked by irradiation under the following conditions give wires suitable for use in automotive cables.

10 - Extruder temperatures (°C):

Z1	Z2	Z3	Z4	Z5	Z6	Head	Die	Screw
150	160	175	210	230	240	240	250	80

- Screw design : Elise
- Extrusion tools : 3 angle die and wire guide
- Speed of the line : 50 m / min

15 - Thickness of the insulating layer : 0.3 mm

- Diameter of the copper core : 0.8 mm
- Temperature of the compound at the entrance of the feed zone : cold (23 °C)
- Temperature of the cooling trough : 60 °C
- Irradiation energy: 20 Megarads

20 4 - Cable properties:

Crosslinking performance (according to IEC 811-2-1):

Hot set test at 200 °C, 20 N/cm² (%): <150%

Mechanical properties before ageing (according to IEC 811-1-1):

Tensile stress at break (MPa)	>12
Elongation at break (%)	>300

5 Winding test after ageing 10 days @ 150°C on copper (according to IEC 811-1-2):

No cracks

Flame test (according to ISO 6722):

Pass

Scrape abrasion resistance (according to ISO 6722):

10 Number of cycles before failure : > 300

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Claims

1. A crosslinkable polymeric composition comprising
 - (a) a blend of:
 - (i) 100 parts by weight of LDPE component (A)
 - (ii) 1 - 200 parts by weight of HDPE component (B) having a polydispersity (Mw/Mn) of < 12.
 - (iii) 0 - 100 parts by weight of an EVA copolymer (C).
- 5 2. A composition according to claim 1 wherein the blend comprises
 - (i) 100 parts by weight of LDPE component (A)
 - (ii) 1 - 100 parts by weight of HDPE component (B) having a polydispersity (Mw/Mn) of < 12, and
 - (iii) 0 - 100 parts by weight of an EVA copolymer (C).
- 10 3. A composition according to either of the preceding claims wherein the blend comprises
 - (i) 100 parts by weight of LDPE component (A) and
 - (ii) 1 - 60 parts by weight of HDPE component (B) having a polydispersity (Mw/Mn) of < 12.
- 15 4. A composition according to any of the preceding claims wherein the blend comprises
 - (i) 100 parts by weight of LDPE component (A) and
 - (ii) 25 - 55 parts by weight of HDPE component (B) having a polydispersity (Mw/Mn) of < 12.
- 20 5. A composition according to any of the preceding claims wherein the blend

comprises

- (i) 100 parts by weight of LDPE component (A) and
- (ii) 35 - 55 parts by weight of HDPE component (B) having a polydispersity (Mw/Mn) of < 12.

5 6. A composition according to any of the preceding claims wherein the HDPE has a polydispersity of < 9.

7. A composition according to any of the preceding claims wherein the HDPE has a polydispersity of < 7.

10 8. A composition according to any of the preceding claims wherein the HDPE has a density in the range 0.940 – 0.960 g/cm³.

9. A composition according to any of the preceding claims wherein the HDPE has a density in the range 0.950 – 0.960 g/cm³.

10 10. A composition according to any of the preceding claims wherein the HDPE has a MFR in the range 2 – 6 g/ 10 minutes.

15 11. A composition according to any of the preceding claims wherein the LDPE has a density in the range 0.926 – 0.940 g.cm².

12. A composition according to any of the preceding claims wherein the LDPE has a density in the range 0.930 – 0.940 g.cm².

13. A composition according to any of the preceding claims wherein the LDPE has a 20 MFR in the range 0.15 – 2 g/10 minutes.

14. A composition according to any of the preceding claims wherein the EVA component (C) has a vinyl acetate (VA) content in the range 1 – 45 % by weight and a MFR in the range 0.1 – 50 g/10 minutes.

15. An automotive cable comprising a crosslinkable polymeric composition

25 comprising

(a) A blend of:

- (i) 100 parts by weight of LDPE component (A)
- (ii) 1 – 200 parts by weight of HDPE component (B) having a polydispersity (Mw/Mn) of < 12.

30 (iii) 0 – 100 parts by weight of an EVA copolymer (C),

(b) An antioxidant system (D) and

(c) A flame retardant material (E).

16. An automotive cable according to claim 14 comprising a crosslinkable polymeric composition as claimed in any of claims 2 to 14.
17. A cable according to claims 15 or 16 wherein the flame retardant material (E) comprises a halogenated material.
- 5 18. A cable according to any of claim 17 wherein the halogenated material is present in amount of 15 – 40 parts per hundred of the polymer blend.
19. A cable according to any of claims 15 - 18 wherein the flame retardant material (E) includes a coagent.
20. A cable according to claim 19 wherein the coagent is present in amount of 6 –
10 20 parts per hundred of the polymer blend.
21. A cable according to claim 19 wherein the coagent is antimony trioxide.
22. A cable according to claims 15 – 21 wherein the antioxidant system (D) is present in amount of 0.2 – 0.9 parts per hundred of the polymer blend.
23. A polymeric composition according to any of the preceding claims crosslinkable
15 by use of a silane, a peroxide or an irradiation crosslinking process.

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INTERNATIONAL SEARCH REPORT

Inte
nal Application No
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A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08L23/06 C08L23/08 C08K3/00 H01B3/44

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08L H01B C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>US 3 956 567 A (KRACKELER JOSEPH J ET AL) 11 May 1976 (1976-05-11)</p> <p>abstract column 1, line 8 - line 14 column 1, line 34 -column 2, line 19 column 2, line 34 - line 58 column 2, line 59 -column 3, line 50 column 4, line 12 - line 17</p> <p style="text-align: center;">-/-</p>	1-9, 11-13, 15-23

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

Int'l Application No.
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 99 65957 A (EGASHIRA TOSHIAKI ; SAKAMOTO KAZUYUKI (JP); WAKAYAMA MASAHIRO (JP);) 23 December 1999 (1999-12-23) abstract & EP 1 153 948 A (JAPAN POLYOLEFINS CO LTD) 14 November 2001 (2001-11-14) abstract page 3, line 5 - line 11 page 6, line 15 - line 18 page 7, line 24 - line 26 page 8, line 3 - line 15 page 12, line 19 - page 14, line 17 page 16, line 55 - page 18, line 55 page 42, line 15 - page 44, line 42 claims 27, 29, 30	1-23
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No.
PCT/IB 01/02742

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